HOCl from EOS MLS on Aura: version 1.5 and preliminary version 2 data comparisons with other measurements and models

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HOCl data from MLS

- MLS measurement discontinuities affect HOCl
  - The 640 GHz radiometer bands 10 and 29
    (mainly affecting ClO and HOCl retrievals, respectively)
    were turned off for a while to better understand potential degradation issues
    > off for 2006 April 8,9,10 and also for April 17 (19:52 UT) through May 17
    → no useful HOCl (or ClO) data for above periods [although L2 files exist]
  - These bands now seem likely to last for nominal mission lifetime (5 - 6 years) and they have remained on since May 18, 2006.

- MLS HOCl requires averaging (e.g. 10° zonal means for > 1 week) to get useful sensitivity (~ 10 pptv or less)

- From last meeting: V1.5 MLS HOCl retrievals were not considered useful in the lower stratosphere (pressure of ~20 hPa and larger)
  - but morphology in upper stratosphere seems reasonable, to first-order
  - lower priority product than others

- Update given here for V2 results and expectations
  - not many days have been reprocessed using V2.1 software

- HOCl global measurements from MIPAS (on ENVISAT) have recently been published *[Von Clarmann et al., JGR, 2006]*
  - Difficult measurement in infrared emission, with contaminant species and “hard-to-see” spectrum – but reduced residuals when include HOCl in fits.
  - MIPAS results are slightly larger than FIRS-2 measurements (older balloon data corrected for time difference and increase in chlorine)
  - MIPAS retrievals are significantly larger than MLS values, but qualitatively similar.

MIPAS HOCl (2002 Sep./Oct.) MLS (Sep. 2004) [16-days] MLS (Sep. 2005)

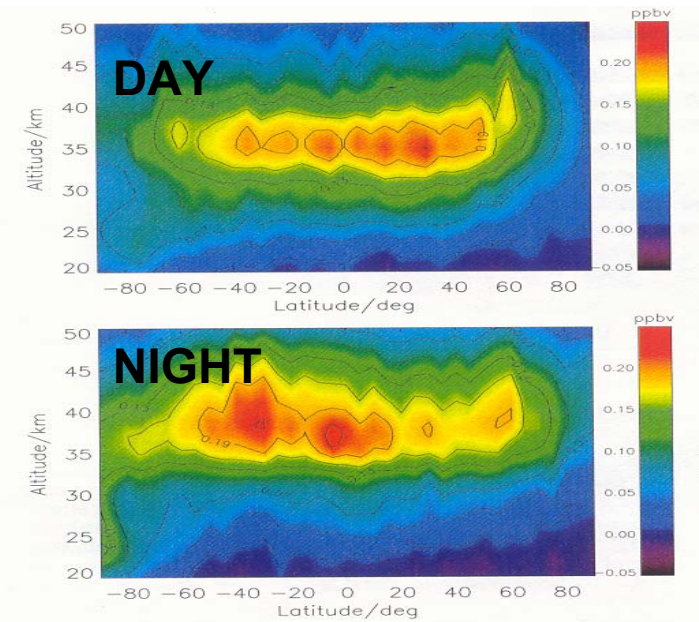
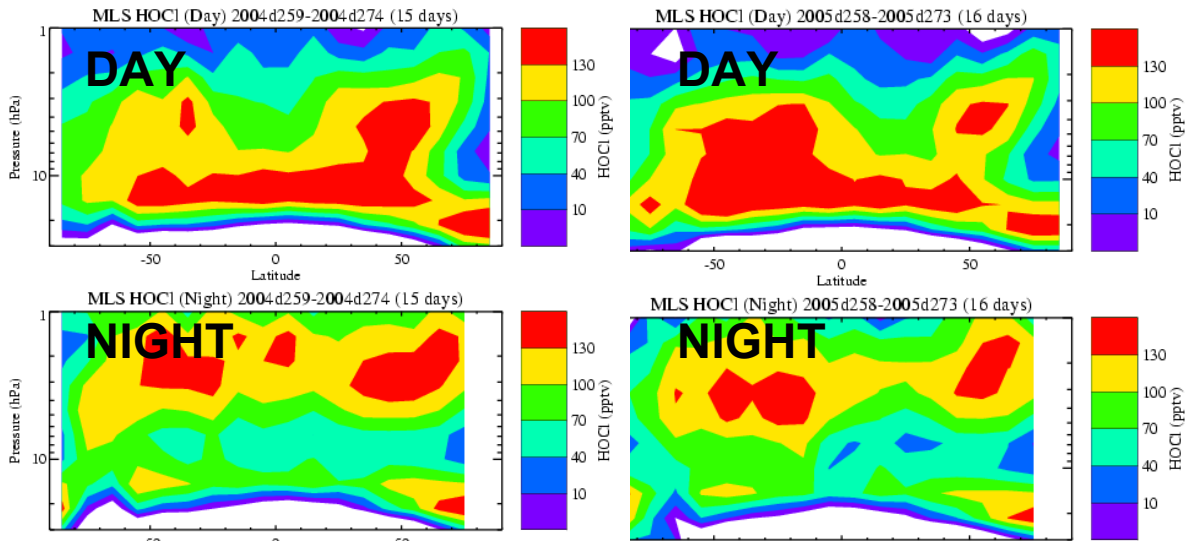
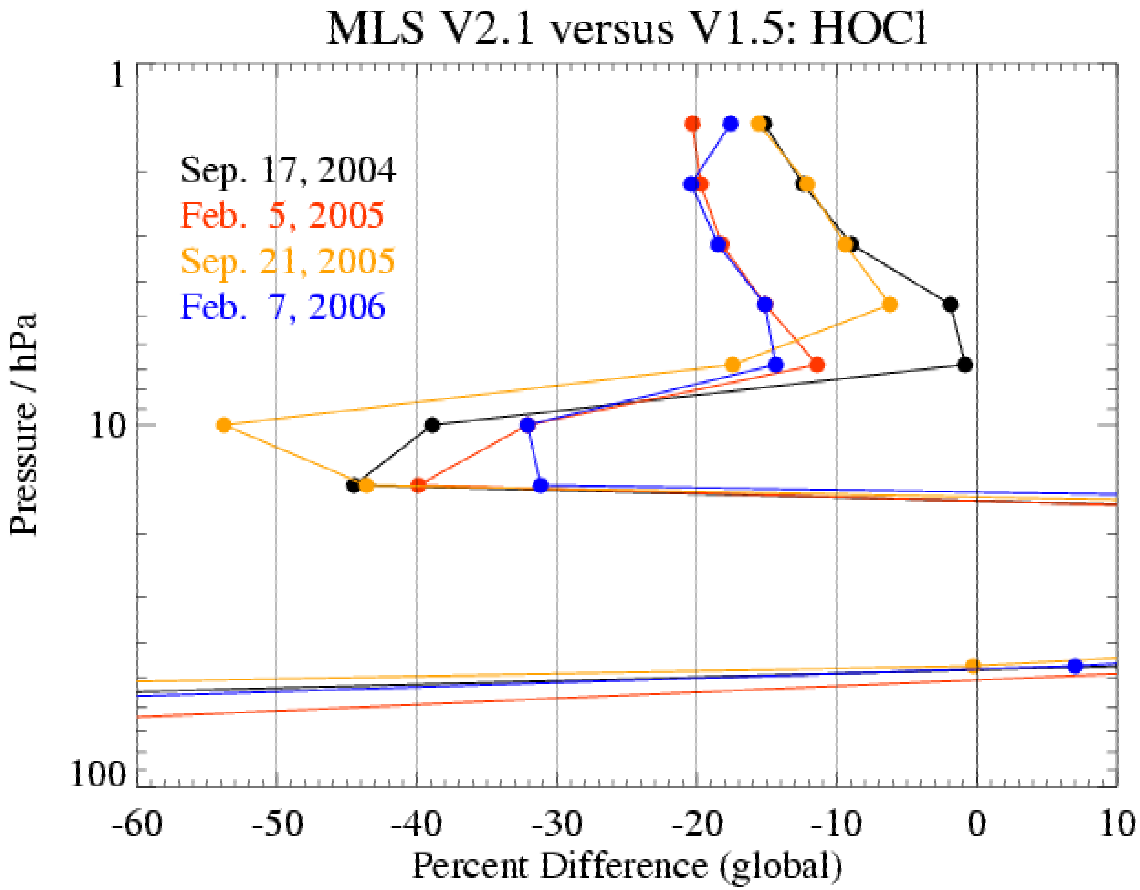


Figure 4. HOCl zonal mean (top) daytime and (bottom) nighttime VMRs, averaged over the episodes 18–27 September and 11–13 October 2002.



MLS V2.1 versus MLS V1.5 data: HOCl

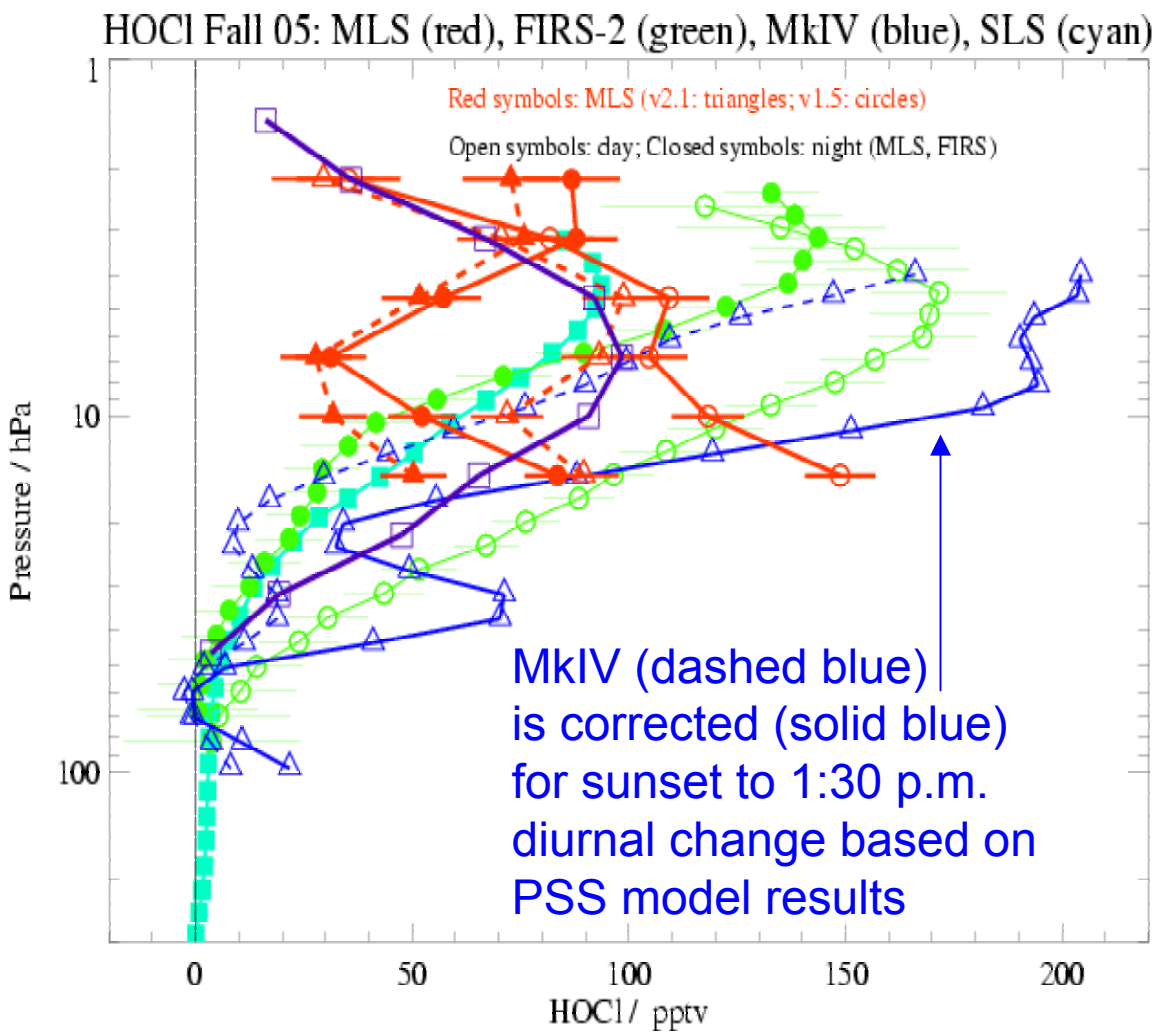


- Changes in HOCl are fairly systematic (but averaging of many profiles required)

- Global average change shows a decrease by ~ 10 to 40% in the upper stratosphere

- No significant improvements in the lower stratosphere (still see large oscillations in the profiles)

MLS HOCl and balloon results



Results from balloon campaign data on HOCl for Sep. 2005 (Ft. Sumner)

- MLS values for v2.1 should decrease roughly as shown on the left (10 deg. zonal means used for 16-day avg. in v1.5 data; crude adjustment shown for v2.1)

- Day/night MLS differences are qualitatively similar to FIRS-2 results, but absolute values are lower for MLS (by ~ 30-50%), and in better agreement with SLS data

MLS HOCl and balloon results: other (simple) model/data checks

- HOCl photochemical equilibrium (simple model – for fun…)

- In daytime equilibrium, expect to see

$$[HOCl]\ (J_1 + k_2\ [O]) = k_1\ [ClO]\ [HO_2]$$

or $[HOCl] = k_1\ [ClO]\ [HO_2] / (J_1 + k_2\ [O])$

where J_1 = J(HOCl) ; photodissociation rate constant for HOCl [s^{-1}]

k's are rate constants (formation and loss)

- We can estimate the daytime equilibrium abundance of HOCl if we have estimates for [ClO] , [HO_2], [O], and the rate constant values (temperature-dependent) [need T]

- As luck would have it… MLS measures ClO, HO_2, and T
(and even OH for small other loss term from OH + HOCl)
and [O] can be obtained from equilibrium with ozone ($J_2\ [O_3] = k_4\ [O][O_2][M]$)

Use J_1, J_2 values from model values for daytime MLS solar zenith angle
(Kovalenko/Salawitch) and k values from JPL recommendations
(+ a few test cases discussed below for k_1)

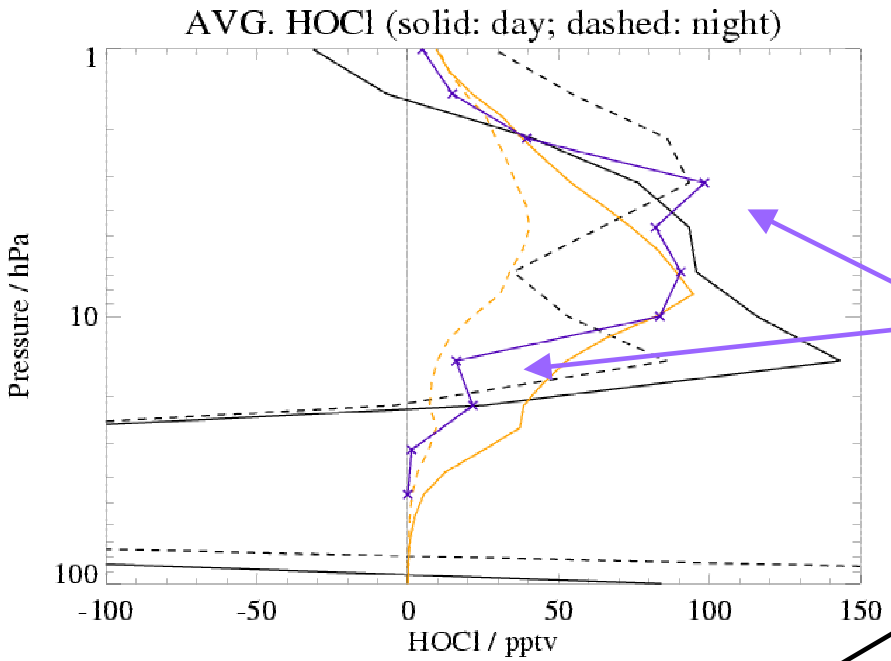
16-day HOCl averages (day and night) for MLS & SLIMCAT near Sep. 20, 2005

solid: daytime dashed: nighttime **black: MLS** **orange: SLIMCAT**

- SLIMCAT

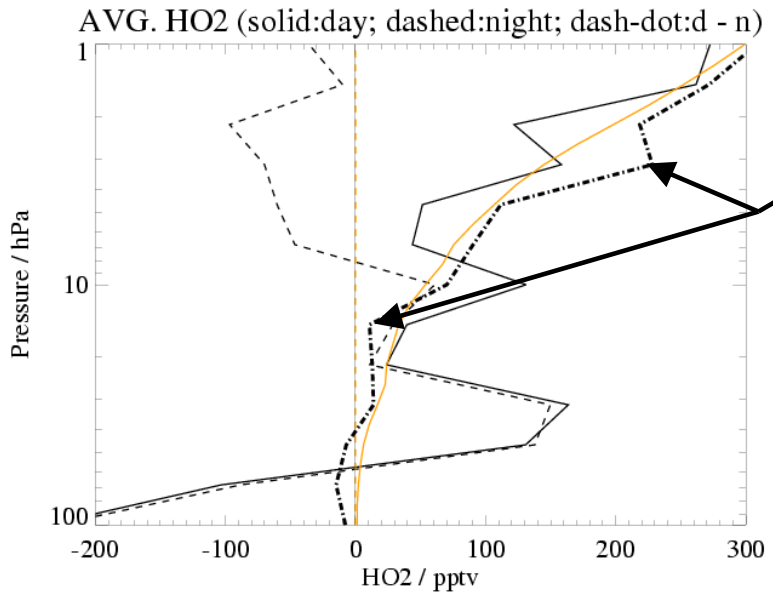
day, solid; night: dashed

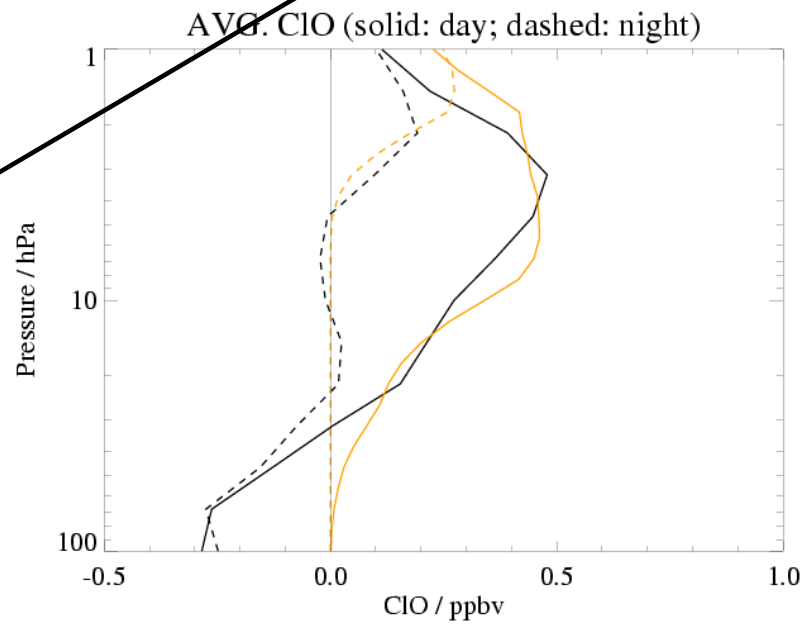
[SLIMCAT values thanks to I. MacKenzie, M. Chipperfield, R. Harwood et al.]

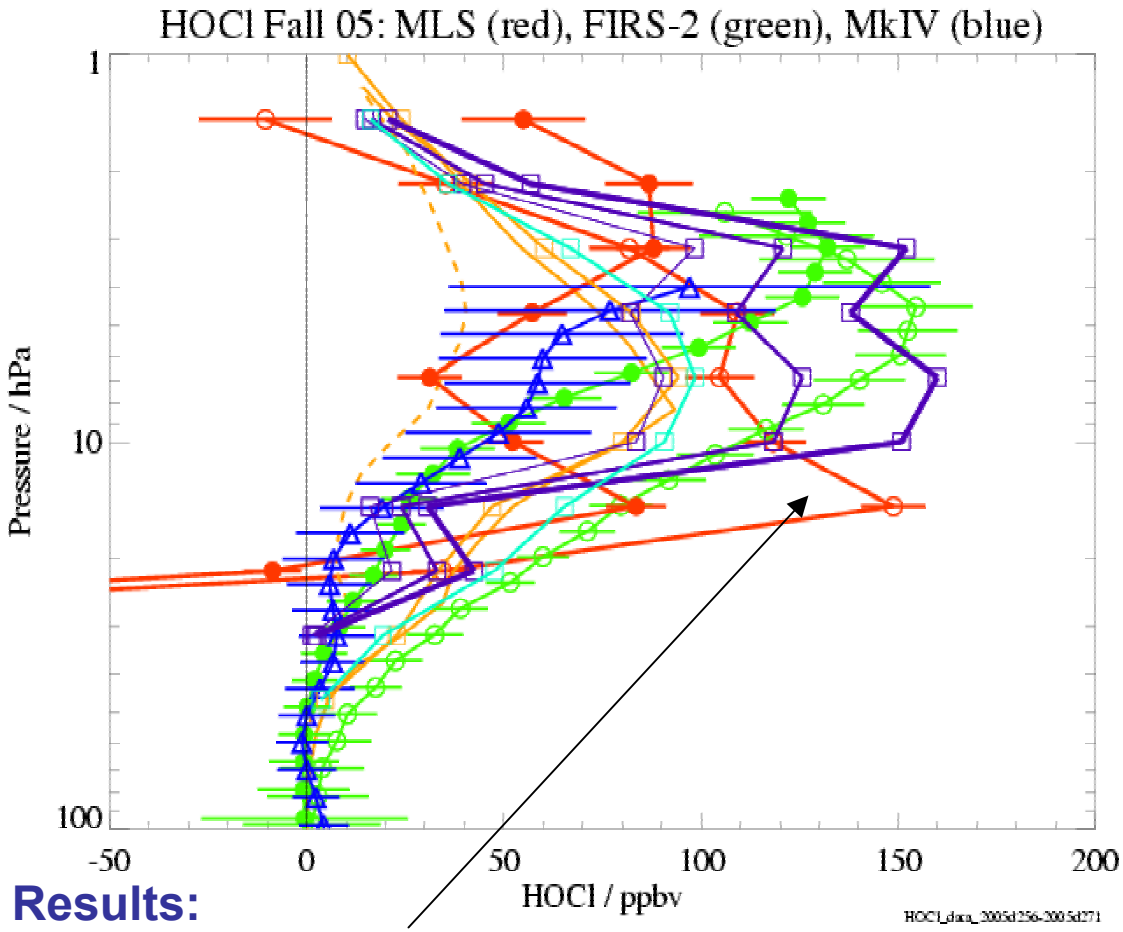


Equilibrium (daytime) model results for HOCl

- Main diffs. from SLIMCAT come from HO_2 (different than SLIMCAT), even if use day-night MLS HO_2.







16-day zonal means (MLS V1.5)
- daytime (open circles)
- nighttime (closed circles)

- **FIRS-2 balloon data day (open); night (closed)**

- MkIV (sunset) (triangles) [older (but July archive) version of MkIV data shown here, lower values]

- Equilibrium results: purple squares
> thin: k_1 ($ClO+HO_2$) [JPL, 2006]
> thick: faster k_1 [JPL, 2000]
> thickest: fastest k_1 [Stimpfle et al., 1979]

- **PSS model (Kovalenko/Salawitch) for Sep. 20/05 (constrained by MLS long-lived species)**

- **SLIMCAT**
day, solid; night: dashed

- **Orange boxes: Equilibrium model HOCl using SLIMCAT values for** ClO, HO_2, O_3, T → **<u>using equilibrium results seems OK</u>**

Results:

> MLS V1.5 has oscillations for P of 10 hPa and larger; but has same general characteristics as FIRS-2
- higher altitude peak for nighttime than daytime and lower night values than day.
> MLS values lower than FIRS-2 (by ~ 30 - 50%); MLS values (and SLS data, not shown here) agree better with slow (JPL 2006) k_1, FIRS-2 (and MkIV) better with faster k_1

Summary and plans: MLS HOCl

- **Summary of validation results**
  - Can use MLS HOCl data (V1.5 and V2) for continued evaluations at pressures from ~ 10 hPa to 2 hPa (revised vertical range)
  - MLS HOCl values are lower (by ~ 30-50%) than FIRS-2 data (and MIPAS data), but agree better with SLS data for Sep. 2005 balloon campaign.
  - Sep. 2004 balloon campaign gives similar results (MLS versus FIRS-2); not updated here.
  - MLS day and night data (averages) show some similarities with FIRS-2 and models
    > night profiles peak at higher altitude
    > smaller daytime abundances than nighttime
  - Uncertainties in rate of formation for HOCl affect model results; the lower values (MLS, SLS) agree better with lower (recommended) rate constant, the larger (FIRS-2) values agree better with a higher rate constant – based on constrained simple daytime equilibrium model or based on PSS model (from Salawitch/Kovalenko).

  > Main MLS issue: improve the lower stratospheric MLS HOCl data quality
    - However, this has lower priority than other potential improvements for MLS
  > Which HOCl rate of formation rate constant is correct (balloon data do not agree)?
    - Slower (recommended) k agrees better with SLS/MLS than with FIRS-2, MkIV (or MIPAS).
    - Sort out balloon differences (?)
- **Validation paper?** Maybe…
  – Radiance averaging approach may give better results, as for BrO (but TBD)
  – A brief report may be worthwhile, but probably worth trying for further improvements before this is done (possibly not before JGR special issue deadline…)